RESEARCH ARTICLE

Biodegradable Hydroxypropyl Methyl Cellulose/Poly (Vinyl alcohol) Blend Membranes as Oxygen Barriers and their Application in Processed Food Packaging

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ABSTRACT: In the present study, the membranes based on Hydroxypropyl methyl cellulose (HPMC) blended with poly(vinyl alcohol) (PVA) with blending ratio of 20:80 (w/w) have been prepared. The blend membranes with same composition but with varied thickness were prepared i.e. 45 and 90 μm. The two variant membranes thus prepared were tested for mechanical strength to assess its tolerance. The membranes used for measuring the oxygen permeability under varying feed pressures (maintaining the preferred gas pressure differential throughout the membrane) in the range from 1 to 10 kg/cm^2 feed pressure. Oxygen permeability of the membranes ranged from 0.1123 to 0.1661 Barrer for 45 μm and 0 to 0.1365 Barrer for 90 μm thick membrane has been recorded with linear increase in feed pressures. Except at 10 kg/cm^2 pressure, the observed oxygen permeability values are almost close to total permeability. Further, the prepared membranes were tested for biodegradability and are found to be biodegradable. The tested membrane could be the best candidate as oxygen barriers and are very useful in the food packaging industries.

KEYWORDS: poly(vinyl alcohol); Blend membranes; permeability; packaging material; Barrier

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1. INTRODUCTION

Membrane-based gas separation is a fast-growing area by helping as one of the major industrial gas separation technologies. The market demand and different emerging applications are increasing because membrane-based gas separation technology gives the number of benefits in terms of energy-saving and cost-effectiveness. The membranes based on the polymer are controlling materials in this area owing to their easy scale-up, excellent processability, and feasibility in various modules. Several inorganic, including carbons, silica, zeolites, ceramics, and metal membranes have been also extensively studied for more specific gas separation applications where polymeric membranes cannot serve [1-3].

The development of novel polymers offering important combinations of high selectivity, high permeability, good mechanical stability, and processability at ambient temperatures and pressures has been quite slow [4-6]. In general, the flexible polymer films have favorable properties like low cost, good barrier properties against moisture and gases, heat sealable to prevent leakage of contents, possess both wet and dry strengths, easy to handle, and add little weight to the final product. Thus, they fit closely to the shape of the food, thereby wasting little space during storage and distribution. In food packaging applications, oxygen barrier properties of the polymers are important, since many food materials require the specific atmospheric conditions to sustain their freshness and quality during the storage. Hence, food materials are increasingly being packed in a protective atmosphere with a specific mixture of gases, thereby ensuring optimum quality and safety of the product. However, to ensure a constant gas composition inside the packaging film, the polymer should have certain specific oxygen barrier properties [7].

Transparent and flexible gas barrier films are key components in food packaging. In most cases, food processors are mainly served by low-density PE (LDPE) and linear low-density PE (LLDPE) [8]. The main problem of polyethylene is its high oxygen permeability. Having a barrier capacity is crucial for plastics films used in the food packaging which favors the preservation of nutritional and organoleptic product qualities. For this purpose, it is necessary to prevent food product losses (aroma, CO2 loss, and loss modified atmosphere) as well as the penetration of

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external gas (oxygen and steam) through plastics [9-11].

Different technologies are developed to supply chemical element barrier to clear films, as PE films, used for packaging applications. The main technologies area unit the following: (1) Coating with high barrier materials, generally inorganic oxide layers (e.g., SiOx or Al_2O_3), these films show optical transparency and very low gas transmission rates at a low thickness (< 100 nm) [12-13] but they tend to form imperfections during deposition, they present low substrate adhesion and when they are flexed are prone to crack. (2) Multilayer films area unit shaped from monolayers; the one that is within maybe a skinny layer of barrier material (e.g. EVOH, polyamide or aluminum) and the outer layers of structural polymers (e.g. PE, PP or PET). Despite their efficacy, a high adherence between the materials is necessary. Besides, another problem is their recyclability due to the use of different types of polymers and adhesives in the same film. Current trends regarding plastic packaging are focused on developing thinner structures with high barrier properties, diminishing raw material. (3) A new alternative to common technologies is the use of clay nanocomposites that improve plastics properties, increasing not only the barrier and mechanical properties but also heat resistance [14]. Getting a complete exfoliation of nanoclays (nanoclay layers are completely separated, with the high surface area) is necessary to obtain proper results using nanocomposites. Moreover, a high affinity between compound Associate in Nursingad clay sheets and also the exfoliation area unit required for adequate dispersion of clays into the polymer achieving these properties [15-16]. Plastic films as a packaging material have several advantages over conventional food packaging. The material is very less proven to contaminate and pilferage. By using plastic as packaging material the shelf life of the food product becomes longer. The materials will give a very attractive texture and is leveraged for the nice branding purposes. The plastic films are very lightweight and very easy to print on its surface. Additionally, the films are very good barrier properties and are recyclable and reusable. The different packaging materials available in the market are high-Density Polyethylene, Low-Density Polyethylene, Polypropylene, Polyethylene terephthalate (PET or PETE), Polycarbonate, Polyethylene naphthalate, Polystyrene, etc [17]

However, since the contact of foodstuff with polymeric films may alter the performance. It is a very important parameter to study the barrier characteristics of the packaging materials under realistic conditions. For instance, there are chances of contaminations like oxygen may cause ripening or rotten of the food materials [18]. The present research work aims to focus further information on the permeability behavior of the polymer films that are used as packaging materials for the food industry.

2. MATERIALS AND METHODS

2.1 Chemicals

PVA (MW 125,000) and HPMC were purchased from s.d. Fine Chemicals, Mumbai, India. All other chemicals were of reagent grade and were used without further purification. Double distilled water was used throughout the research.

2.2 Synthesis of dense blend membranes

The blending of polymers was completed in aqueous media. The two different polymeric membranes with same concentration and same synthesis conditions but different membrane thickness were prepared. The 2:6 ratio of HPMC/PVA was dissolved in water under constant stirring at ambient temperature until the homogeneous thick viscous slurry was obtained and this solution was filtered. The obtained homogeneous slurry was cast on to a clean and dry glass plate by using doctors knife with pre adjusted thickness. The two different dense membranes with thickness i.e. 45 and 90 μm were prepared and are named as P-45 and P-90.

2.3 Permeability Measurements

The permeabilities study with single gas for O_2 was evaluated by gas permeameter for the prepared dense membranes. The permeameter consists of a stainless steel permeation cell which separates upstream (feed side) and downstream (permeate side). A pressure transducer is connected to the downstream side to measure the pressure change with time in the permeate side. This cell exposes a membrane area of 13.302 cm^2 to the gas. The membrane separation follows the solution diffusion modem and it involves sorption at the top side of the membrane and diffusion across the barrier and finally desorption at another side of the membrane. The schematic of gas permeation unit diagram is shown in figure 1.

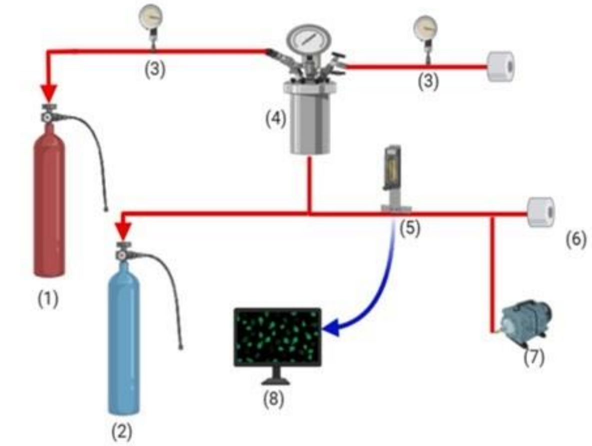
The constant-volume variable pressure method was used to measure the permeation of the pure gas. The pressure increase with time was plotted from the raw data. The gas permeability is calculated based on the following equation:

$$P = \frac{Vl}{A}\frac{T_0}{P_f P_0 T}\left[\left(\frac{dp}{dt}\right)_{ss} - \left(\frac{dp}{dt}\right)_{leak}\right]$$

Where:

- P is the permeability of the gas through the membrane (barrer), (1 Barrer = 10^{-10} cm3 (STP) cm cm^{-2} s^{-1} $cmHg^{-1}$).
- V is the permeate volume (cm^3).
- l is the thickness of the membrane layer (cm).
- A is the effective area of the membrane (cm^2).

The ideal selectivity $\alpha_{A/B}$ of gas pairs, A and B, was calculated. It is defined as the ratio of their permeably:



(1)Oxygen gas cylinders, (2) Helium gas cylinders, (3) Pressure gauge (4) Membrane gas permeate unit (5) Pressure transmitters (6) Gas chromatography (7) Vacuu pump and (8) Output unit.

Figure 1: Schematics of the gas separation unit.

2.4 Mechanical properties

The mechanical properties of the blend polymeric membranes such as tensile strength (MPa) and elongation at break (%) were studied by universal testing machine (UTM) (Hounsfield, UK), model H 25 KS, with an operating head load of 5 kN, were measured for all the prepared films according to the test method ASTM D 412. Membrane strips were placed between grips of the testing machine. The grip length was 5 cm; while the speed of testing was set at 5 mm/min. Tensile strength was calculated using the equation:

$$TensileStrength = \frac{Max\ Load}{Cross\ Sectional\ Area} \quad (1)$$

2.5 Scanning Electron Microscopy (SEM) Studies

Surface morphology of P-45 and P-60 film matrix was evaluated with a Scanning Electron Microscope; model Jeol, Model 7900F after sputter coating of gold on the specimen surface.

3. RESULTS AND DISCUSSION

3.1 Transparency

The prepared membranes were transparent in nature and the membranes were homogenous and odorless. The membranes were flexible and even after bending they sustain their original form as anticipated because of the internal hydrogen bonding and increase the intermolecular spacing, membranes were became transparent and flexible.

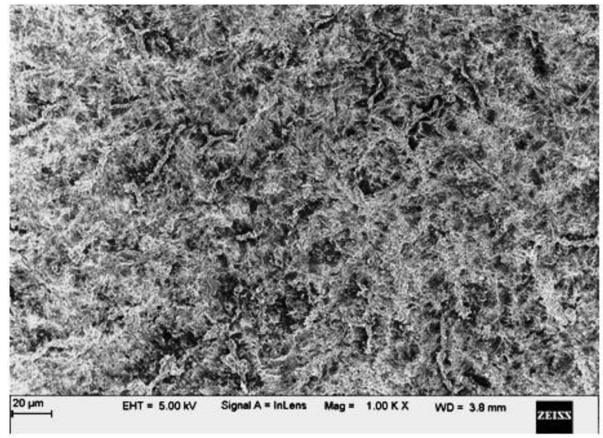


Figure 2. SEM images of HPMC/PVA blend membrane

SEM image of the surface of the pristine HPMC/PVA is shown in figure 2. From the SEM images, it is observed that the SEM image is that both HPMC and PVA are compatible and were homogeneously blended each other.

3.2 Mechanical properties

Mechanical properties were performed for all the polymeric membranes as per ASTM D 412 and are tabulated in Table I. Tensile strength is highest for P-90 as compared to P-45., while on the other hand the same trend was continued with ultimate elongation is least for P-45 and increases in the order P-90. This property may be due to increased flexibility of the membrane materials as the increased thickness of the polymer matrix.

Table I: Mechanical property of all polymeric membranes

Polymer	Tensile strength MPa ± S.D	Ultimate elongation ± S.D
P-45	80.3 ± 0.4	1211.3 ± 0.3
P-90	131 ± 0.7	1431 ± 0.2

3.3 Degradation Test

Weight losses due to soil burial treatment of the P-45 and P-90 membranes were performed. The test results revels that the addition of HPMC has decreased the weight losses of the films compared to the plain PVA membrane. The weight losses are much affected by the composition of the mixture. The highest values of weight loss were recorded for the M-90.

3.4 Gas Permeability Studies

The prepared membranes were evaluated for the oxygen gas permeability. The permeability test was performed for O_2 with the prepared P-45 and P-90

membranes (i.e. 45 and 90 μm thickness). The permeability values for the tested gases are tabulated in Table II.

Table II Effect of Feed Pressure on Oxygen Permeability at 25°C.

Pressure Applied (kg/cm²)	Permeability K (Barrer)	
	P-45	P-90
1	**0.1123**	**0**
1.5	0.1324	0.114
2	0.1521	0.1341
2.5	0.1564	0.1379
5	0.1621	0.1431
10	0.1661	0.1365

1 Barrer = 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cmHg^{-1}

3.5 Membrane performance

Membranes were tested for oxygen permeability by varying the feed pressures (maintaining the desired pressure differential across the membrane) and thickness of the membranes. The permeability (K) values are plotted in figure 3. In case of M-45 membrane, the pressure was increased from 1 to 10 kg/cm^2. At 1 kg/cm^2 pressure, the permeability was 0.1123 Barrer, which has increased to 0.1324, 0.1521, 0.1564, 0.1621and 0.1661 at 1, 1.5, 2, 2.5, 5 and 10 kg/cm^2 feed pressures respectively. Whereas the M-90 membrane shown zero permeability from the pressure 1 kg/cm^2 and 0.114, 0.1341, 0.1379, 0.1431 and 0.1365 for the corresponding pressure i.e. 1, 1.5, 2, 2.5, 5 and 10 kg/cm^2 respectively. Even at high pressures the prepared membranes have shown a very poor permeability towards oxygen. Hence we may conclude that these are the better candidates for the packaging of processed food since oxygen is the main component which will spoils the shelf life of the same.

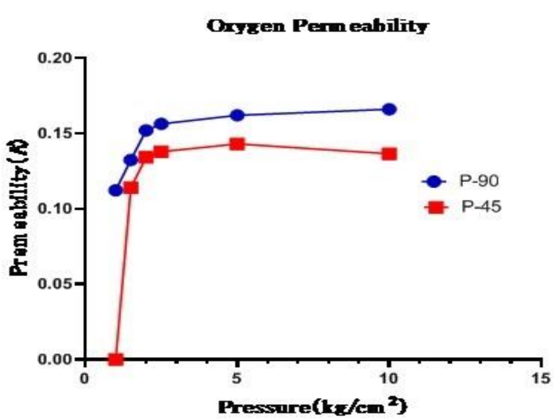


Figure 3: Effect of Feed Pressure on Oxygen Permeability at 25°C.

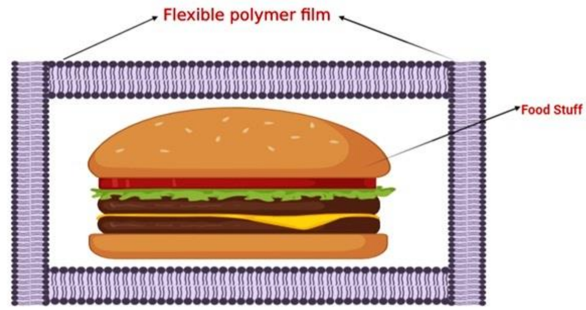


Figure 4: Illustration of the food packed in the flexible polymeric film.

The schematic diagram of the packaging material used in the packaging of processed food was illustrated in figure 4. As the COVID-19 outbreak has spread across the globe and its humanitarian collision has increased, industries that help provide for essential needs, such as getting food and required supplies safely to consumers, are increasingly affected. The food packaging in the packaging industry's largest area of activity is greatly affected. It is necessary to develop food packaging materials that act as antiviral in nature.

CONCLUSION

The effort to study the oxygen barrier property was shown very efficiently by preparing the blend polymeric membranes. The HPMC/PVA blend membranes efficiently acted as the oxygen barriers. The transparency of the membrane was very good and its mechanical strengths were excellent. The biodegradability of the M-90 membrane is good and is the best candidate for the packaging of processed food materials.

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